# COARSENING IN SOLID-LIQUID MIXTURES-2

# SCIENCE REQUIREMENTS DOCUMENT AND ADDENDUM

June 19, 2000


Addendum to the Science Requirements Document

Addendum to the Science Requirements Document

# Coarsening in Solid-Liquid Mixtures – 2
# (CSLM-2)

Principal Investigator: P. W. Voorhees
Department of Materials Science and Engineering
Northwestern University
Evanston, IL 60208
Tel: (847) 491-7815
FAX: (847) 491-7820

October1998/Rev. June 2000

Signature Page for
Microgravity Science Division
**Science Requirements Document (SRD)**

Title of Experiment: Coarsening in Solid-Liquid Mixtures - 2 (CSLM-2)

Date: April 19, 2000

Revision: 1

4/21/00

Peter W. Voorhees, Principal Investigator
Department of Material Science and Engineering
Northwestern University
Evanston, Il 60208-3111

**CONCURRENCES**

**NASA Glenn Research Center**

Walter B. Duval
Project Scientist
Signature
4/21/00
Date

J. Mark Hickman
Project Manager
Signature
4/20/00
Date

**NASA George C. Marshall Space Flight Center**

Ronald A. Schlagheck
Materials Science Program Manager
Singature
6/7/00
Date

Donald C. Gillies
Materials Science Lead Scientist
Signature
6/7/00
Date

**NASA Headquarters**

Michael J. Wargo
Materials Science Enterprise Scientist
Signature
6/16/00
Date

**APPROVAL**

Bradley M. Carpenter
Enterprise Lead Scientist
Signature
20 June 2000
Date

This Science Requirements Document for Coarsening in Solid-Liquid Mixtures-2 (CSLM-2) is divided into two sections. The first section discusses the results of the CSLM experiments, the need for an additional microgravity experiment, and gives a new set of science requirements. The second section is the Science Requirements Document for the original CSLM experiment. The supporting information for the experiment can be found in this section. The original science requirements document also serves to illustrate that CSLM-2 is within the objectives of the original CSLM experiment.

June 19, 2000

# 1 A Reflight for CSLM

The Coarsening in Solid Liquid Mixtures experiment was flown on STS-83 and STS-94. We performed 7 coarsening experiments on STS-83, and 9 on STS-94. A considerable amount of data was acquired from these experiments. All totaled, approximately 25,000 micrographs have been taken. In the course of performing these experiments a great deal has been learned about the system and its behavior in a microgravity environment. The success of these experiments shows clearly that Pb-Sn solid-liquid mixtures, along with a microgravity environment, can be used to obtain unique data on the coarsening behavior of two-phase systems. It is also clear, however, that some of the objectives of the CSLM experiment were not achieved.

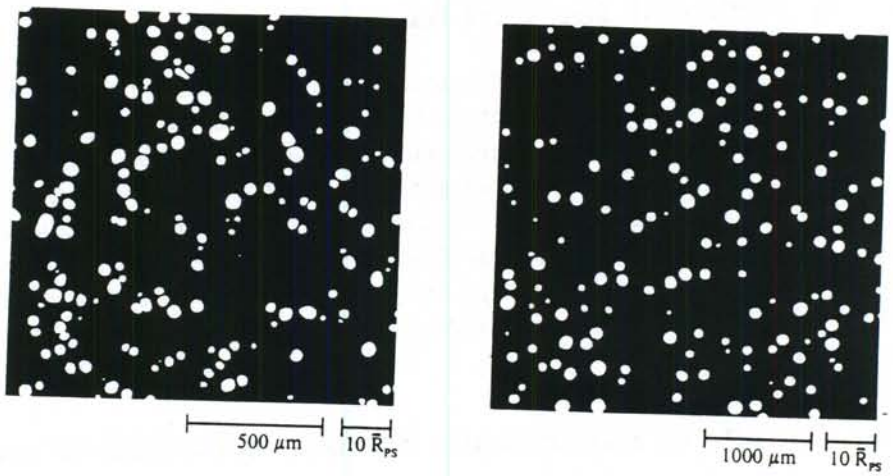
## 1.1 Results of Experiments Performed on STS-83 and STS-94

Most importantly, the experiments have shown that solid-liquid mixtures consisting of Sn-particles in a Pb-Sn eutectic liquid processed in microgravity are ideal systems in which to study the coarsening process. The microstructures of the 10% volume fraction solid samples show nearly spherical, uniformly distributed, solid particles, see fig. 1. This result is of central importance as it indicates that performing experiments in space using the Pb-Sn system will enable us to produce the long-awaited data that can serve as a test of the theories of Ostwald ripening.

In addition to the Ostwald ripening experiments, we performed experiments to determine the temporal evolution of grain boundary grooves. These experiments provided a measurement of the entire thermophysical parameter dependent portion of the coarsening rate constant, in particular, the product of the solid-liquid interfacial energy and the solute diffusion coefficient in the liquid. We find that within the scatter of the data the grain boundary grooves develop at the same rate in microgravity as on the ground. Thus, we can conclude that the ground-based data originally taken by Hardy were not influenced by convection of the liquid.

The most successful series of experiments were those using samples with a 10% volume fraction of solid. This is quite fortunate as virtually all theories for Ostwald ripening make predictions at this volume fraction. A detailed description of the experiments is given in the preprint of a paper, see Appendix 1. A summary of the results of the experiments using a 10% volume fraction of solid is given below:

- The experiments showed unambiguously that the system was coarsening via a transient Ostwald ripening process. This was detected by observing changes in the scaled particle size distribution, see fig. 2, and the radial distribution function during coarsening. This transient state was far longer than was observed in the 70-80% volume fraction solid experiments that were performed on the ground.




(a) (b)

Figure 1: Microstructures of the solid-liquid mixture after (a) 880s of coarsening and (b) 36600s of coarsening. The particles are white and the matrix is black.

- These experiments produced the first measurement of the radial distribution function in a system with sufficiently low volume fraction that it can be compared to theory, see 1.1. This result exceeded our expectations, as prior to flight we were concerned that the solidification process would disturb the spatial arrangement of the particles. It clearly does not on the length-scales sampled in the experiments.

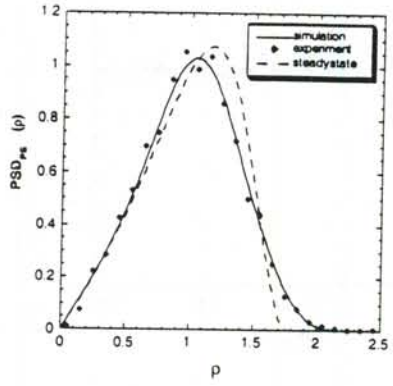
- The absence of gravitationally induced sedimentation allows us to make measurements of the steady state coarsening kinetics with unprecedented accuracy, far better than on the ground. The absence of sedimentation along with the large number of particles measured in the experiments allowed us to identify the presence of transient Ostwald ripening.

- The near-DC microgravity levels are sufficiently small that coarsening experiments for much longer times can be performed than were previously thought possible.

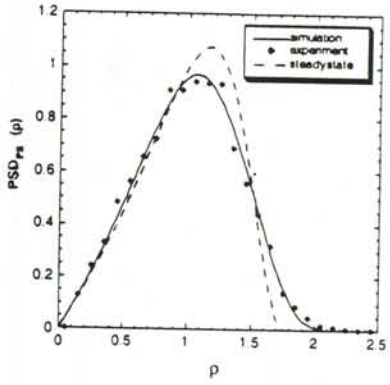
- The scaled particle size distributions are similar to those predicted by theories of transient coarsening, see fig. 2. The coarsening rate is slightly higher than that predicted by theory. The particle size distributions are, however, the first experimentally measured distributions that are close to those predicted theoretically.

The major conclusion drawn from these experiments is that the theory for Ostwald ripening is sound.

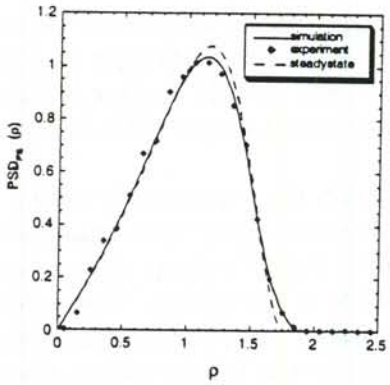
Analysis of samples with higher volume fractions of solid show that the rate constant increases with the volume fraction of solid. However, only a limited number of samples




(a) PSD at 880s and the steady state PSD




(b) PSD at 2280s and the steady state PSD




(c) PSD at 36600s and the steady state PSD

Figure 2: Experimentally measured and calculated particles size distributions using a time dependent theory for Ostwald ripening. $\rho = R_{PS}(t)/\overline{R}_{ps}(t)$, where $R_{PS}$ is the radius measured on a plane of section and $\overline{R}_{ps}(t)$ is the average particle radius measured on a plane of section.

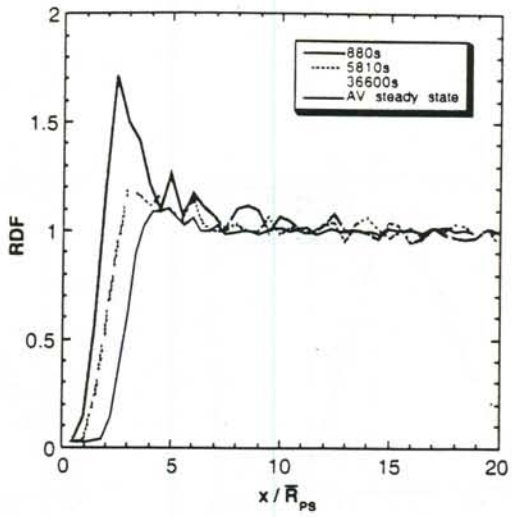



Figure 3: Radial distribution function (RDF) for four different coarsening times. The distance from a particle center is, $x$.

could be used to determine the steady state coarsening kinetics in these samples. Thus it is not possible to determine conclusively the steady state coarsening kinetics in these systems. Finally, experiments using an extremely low, 5%, volume fraction of solid showed that it is in principle possible to perform experiments using samples with volume fractions less than 10%.

With the exception of the 24 hr experiment, the experiments using a volume fraction of 10% solid were extremely successful. In contrast, many other samples showed anomalous microstructures that rendered these unusable. Figure 4 shows the microstructure of sample with a 20% volume fraction solid after 36600s of coarsening. These elongated grains were cause by a temperature gradient in the furnace. Temperature gradients also led to a spatial variation in the volume fraction of solid in the higher volume fraction samples. The effect of the temperature gradient on the coarsening process increases with coarsening time. Thus, many samples coarsened for times less than 2 hrs were satisfactory, but most samples coarsened for times in excess of 2 hrs were unusable.

Temperature gradients were identified as the source of the microstructural anomalies through both experiments and theory. Specifically:

- For STS-94, we moved a 10% sample from the center hole, likely the most isothermal location in the furnace, to an outer hole, and a 20% sample from an outer hole to the center hole. This was done in the two furnaces that were used for the 4 and 10 hour coarsening experiments. We found that when both the 10% and 20% volume fraction samples were placed in an outer hole they exhibited a higher coarsening rate than when they were located in a center hole. Elongated grains were also present near the surface

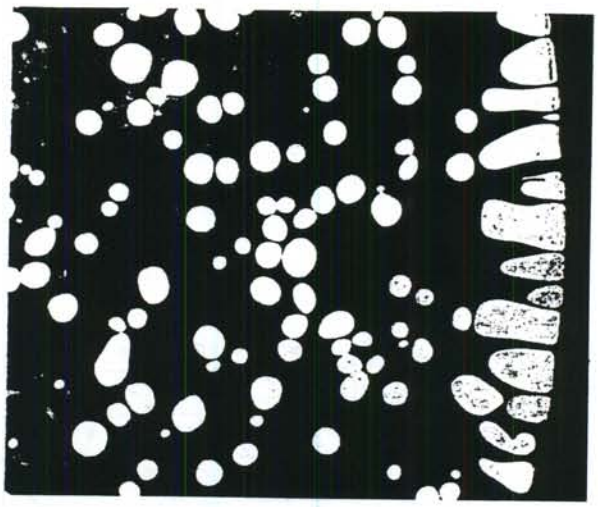


Figure 4: Microstructure after 36600s of coarsening for 20% volume particle phase. The elongated grains are present along the outer surface of the sample.

of the samples located in the outer holes.

- Most samples exhibited elongated solid particles near the surface of the samples at coarsening times in excess of 2 hrs. The elongated grains were not present in samples coarsened for shorter times.

- A model for coarsening in the presence of a temperature gradient was developed and implemented within the point source and dipole approximation for the multiparticle diffusion field. We find that, consistent with the above observations, a temperature gradient can increase the coarsening rate of the entire sample and lead to an increase in volume fraction in the colder regions of the sample and a decrease in volume fraction in the hotter sections. The theory also shows, again consistent with the experiments, that the effects of a temperature gradient increase as the coarsening time increases. A description of the theory for coarsening in the presence of a temperature gradient is given in Appendix 2. In addition, and of central importance for a reflight, a dimensionless quantity was identified that can be used to provide an estimate of a temperature gradient that is sufficiently small that it not affect the coarsening process.

We also found that in the 10% volume fraction samples for very short coarsening times, $t < 400s$, the volume fraction of solid was not the equilibrium value. This is a result of the kinetics of the solute diffusion controlled melting process. This equilibration process was found to be much slower in space than on the ground, and is likely due to a lack of convection in the liquid in the spaceflight experiments. Additionally we found that in the time range from 0 to 400s the temperature shows a monotonic change with time. This results in a temporal variation of the matrix concentration that is of the same order as the change

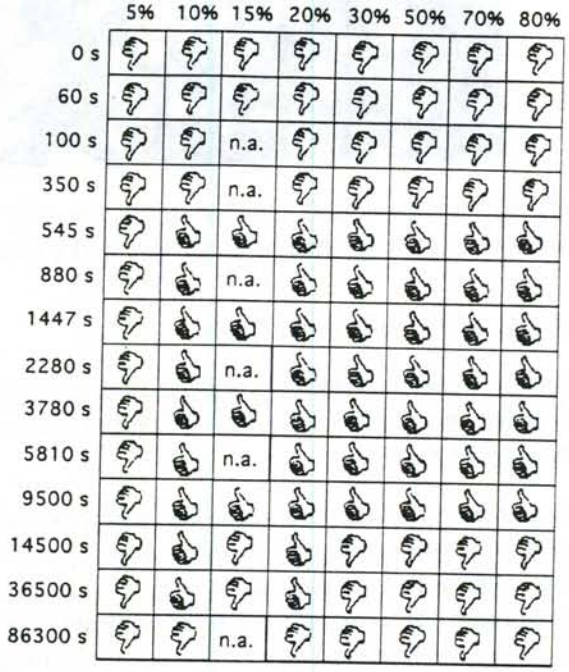



Figure 5: A listing of all the samples processed in space. A thumbs-up denotes a sample that provides useful coarsening data, a thumbs-down denotes a sample that cannot be used to determine the coarsening behavior of the system. n.a. denotes experiments that were never performed.

due to the Gibbs-Thomson effect. A complete listing of all the samples processed in space showing their success is given in fig. 5.

The hardware performed, for the most part, as expected. The furnaces produced an extremely stable, reproducible, thermal environment. We thus feel that experiments using samples with volume fractions less than 10% solid are possible. The quench rates were more than sufficient to produce clearly delineated particles. This was the case even in the furnaces whose quench rate did not meet the science requirements. This indicates that the quench rate given in the original Science Requirements Document can be relaxed somewhat. The temperature gradients in the furnace, however, were unacceptable for coarsening times in excess of 2 hrs for all holes except the center hole.

Finally, the effect of the residual gravitational accelerations on the particle locations has been examined in an effort to ensure that particle movement during the experiments was small. The g-jitter, measured using SAMS, and the near-DC accelerations, measured using OARE, for the STS-94 flight have been used to determine the maximum displacement of a particle of the average size during a 10-hour experiment. In both cases the maximum displacement is a small fraction of the average particle size, indicating that experiments that are much longer than was previously thought possible are feasible.

## 1.2 A Reflight

CSLM-2 is necessary because:

- The CSLM data is insufficient to determine accurately the manner in which the ripening kinetics, particle size distribution and microstructure varies with the volume fraction of coarsening phase.
- The transient coarsening process was much longer than expected, based upon our experience high volume fraction solid ground-based experiments. Thus longer coarsening times are required. We may be able to reach steady state coarsening in the higher volume fraction samples.

## 1.3 Objectives

The objectives of CSLM-2 are identical to that of CSLM. The objectives are to:

- Produce coarsening data which, for the first time, can be compared directly to theory with no adjustable parameters.
- Investigate the factors controlling the morphology of solid-liquid mixtures during coarsening.

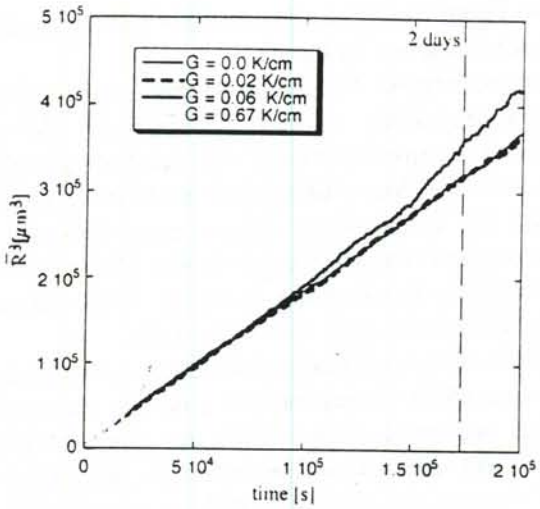



Figure 6: In the absence of a temperature gradient the cube of the average particle radius is a linear function of time. Temperature gradients cause a deviation from linearity in this plot. A temperature gradient of 0.02K/cm does not influence the coarsening process for coarsening times less than 48hrs.

## 1.4 Science Requirements

Most of the science requirements are identical to those of CSLM. There are, however, two major changes: coarsening times to be employed in the experiments and the isothermality of the furnaces.

It is clear from the 10% volume fraction solid CSLM experiments that the steady-state coarsening regime has not been attained. This implies that it is necessary to employ longer coarsening times than those used in the CSLM experiments. In addition, some of the samples coarsened for times in excess of 2 hours did not yield good data due to temperature gradients. Thus the coarsening times that will be employed in CSLM-2 are all greater than 2 hours. The data obtained in CSLM for coarsening times in the interval $400s \leq t \leq 2hrs$ are valid. This CSLM data will be combined with the data taken in CSLM-2 to produce a data set that spans an extremely large average size-scale of the microstructure. For example in the 10% volume fraction samples, we hope to obtain a factor of 5 change in the average particle size by combining both sets of data. This will allow us perform experiments closer to steady-state. Since the data from CSLM and CSLM-2 will be combined, it is essential that the state of the system at the beginning of coarsening for the CSLM-2 experiments be very similar to that of the CSLM experiments. CSLM-2 will employ slightly larger specimens, not so large so as to change radically the thermal environment during processing but sufficiently large to accommodate the larger average particle size.

The temperature gradients necessary to ensure a successful coarsening experiment can be estimated from the theory for coarsening in the presence of a temperature gradient. Us-

ing the particle size at the beginning of coarsening found in the CSLM experiments. fig. 6 shows that a temperature gradient less than 0.02K/cm is necessary to complete a successful coarsening experiment. This value must be viewed as an estimate, however, given that the theory assumes a specific form for the temperature field in the system. Since such temperature gradients are very difficult to measure, ground-based coarsening experiments will be performed to determine if the furnaces are sufficiently isothermal. If elongated grains and/or nonuniformities in the volume fraction are not found in the ground-based experiments the furnaces will be deemed to be sufficiently isothermal for use in a the spaceflight experiment. Since the major reason for the presence of temperature gradients is the nonuniform heat loss from the furnace to the environment, which is largely due to convection on the ground, temperatue gradients will be smaller in space. These ground-based experiments will thus provide an upper bound on the temperature gradients expected in the samples in space.

There is the possibility that part of the disagreement between theory and experiments found in the coarsening rate is due to impurities in the alloys used in the measurement of the materials parameters by Hardy. We will thus also perform ground-based grain boundary groove experiments in purer alloys than were used by Hardy. These experiments will be done in the NASA supplied prototype flight furnace.

Below are the science requirements. Significant changes in the science requirements from those used in the CSLM experiments are emphazised.

## 1.5 Sample

### 1.5.1 Dimensions (Each Sample at room temperature)

*Right circular cylinder with nominal dimensions of 12mm diameter and 6.5mm height.* The exact dimensions will be chosen for the actual cartridge design to guarantee that there is nearly no free volume in the sample holder when the samples are in the solid-liquid state.

### 1.5.2 Solid volume fractions

0.05, 0.1, *0.15*, 0.2, 0.3, 0.5, 0.7, and 0.80 at 185.0°C. The sample-to-sample variation in the volume fraction can be no more than 0.01. The average particle radius can be no larger than $20\mu m$ after 2 min. of coarsening.

### 1.5.3 Coarsening times

*5810, 14600, 36600, 86400, 122400, and 172800 seconds*, equivalently: 1hr 37min, 4hr 3min, 10hr 10min, 24hr, 34hr, and 48hr. *The time $t = 0$ is defined as the time at which the control temperature sensor reaches 184.5°C*

### 1.5.4 Test Matrix

| Time | Volume Fraction | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 5% | 10% | 15% | 20% | 30% | 50% | 70% | 80% |
| 5810s | - | x | - | x | x | - | x | - |
| 14600s | x | x | x | x | x | x | x | x |
| 36600s | x | x | x | x | x | x | x | x |
| 86400s | x | x | x | x | x | x | x | x |
| 122400s | x | x | x | x | x | x | x | x |
| 172800s | x | x | x | x | x | x | x | x |

## 1.6 Containment

No crucible required inside cartridge. *The material in contact with the specimens must be the same as that used in the STS83 and STS94 mission.*

### 1.6.1 Identification

*No indent mark will be used to identify each sample. The samples will be marked during the unloading process.*

### 1.6.2 Separation

Adjacent sample materials within cartridge must not be permitted to mix or touch in liquid state or to leak to the outside to the extent that free-volume within the sample is produced. Ideally, no free surfaces should exist in the sample holder when samples are in the liquid state.

### 1.6.3 Free Volume Control

*The free-volume for each sample at 185°C must be less than 0.1% of the sample volume. The samples must not overfill the crucible in order to avoid contact between the samples during coarsening.*

### 1.6.4 Atmosphere

NASA is free to determine the atmospheric pressure and composition of the gas in the mounting rig, but two criteria must be satisfied. First, the atmosphere must not react in any way with the sample and furnace material, second, the atmosphere must not result in an increased solubility of gas in the solid-liquid mixture as compared with samples prepared on earth in air. No special gases and/or gas pressure are required within the sample holders, but cartridge environment is subject to all specifications described in this requirements section.

## 1.7 Pressure

The coarsening process is relatively insensitive to the level of the pressure.

## 1.8 Post-Flight Deliverables

All the samples flown in space, all the temperature-time data from the furnaces, the furnace temperatures pre-, and possibly post-, flight, and acceleration data determined in conjunction with the Principal Investigator Microgravity Service Group during the times the experiments were performed.

## 1.9 Success Criteria

- Minimal successful: valid coarsening data for volume fractions 10%, 20%, 30%, and 70% at times 5810s, 36600s, 122400s, 172800s.
- Comprehensive successful: valid coarsening data for all volume fractions at all coarsening times.

## 1.10 Thermal Control

### 1.10.1 Heatup Rates

*From 30°C to the start of thermal arrest in no more than 450 sec.* The duration of the thermal arrest can be no more than 180 sec for any individual sample and the change in temperature from the end of thermal arrest to the setpoint temperature, see section 5.4.2 of the original SRD for the definition of the setpoint temperature, must be attained such that:

1. there is no overshoot in temperature of the samples, i.e. no temperature in excess of the upper bound of the setpoint temperature.
2. the post-melt equilibration period, i.e. the time in which the temperature rises from the end of thermal arrest to 185°C, occurs within no more than 180 sec.
3. the temperature gradient in the sample during melting is less than $1.0 K/cm$ to minimize convection during melting.

*It is important that the heatup behavior of the furnaces be such that at the beginning of the coarsening regime the microstructures are similar to those of the STS-83 and STS-94 missions.*

### 1.10.2 Isothermal Soak

The true temperatures at each point within each sample can be no less than 184.7°C and no greater than 185.1°C. *The samples must produce microstructures that are uniform and free of any elongated grains after coarsening for 48 hours. The temperature gradients necessary to achieve this are estimated to be less than 0.02K/cm.* The temperature fluctuations can be no larger than ±0.1K. Furthermore, the temperature variation from a sample at a given volume fraction to another sample at the same volume fraction can be no more than 0.1K. See section 5.4.2 of the original SRD for details.

### 1.10.3 Cooldown (Quench) Rates

*After the quench is engaged and the temperature begins to drop it has to decrease from 185°C to 140°C in no more than 5s, from 140°C to 50°C in no more than 4 minutes and from 50°C to 40°C in no more than 5 minutes.* We require a temperature gradient of less than 100K/cm during the quench period to prevent particle displacement due to convection.

### 1.10.4 Shuttle/Station Environment

We require access to all the measured environmental parameters, e.g. temperature, g-jitter, of the shuttle/station and the unit which holds the furnace.

### 1.10.5 Pre-Experiment Storage

Sample temperature not to exceed 30°C. The delivery of samples to NASA must be less than or equal to launch minus 64 days. The group at Northwestern is responsible for loading the samples in the cartridges. Sample storage prior to experiment should be no longer than 100 days.

### 1.10.6 Post-Experiment Storage

Sample temperature not to exceed 30°C. The samples must be removed from the Shuttle within 1 day after landing. *After unloading the samples they will be stored at −80°C. Twenty days of storage at 30°C after the experiments have been performed will render the samples unusable. However, the storage time at 30C must be as short or possible, specifically: the condition of the sample is excellent if stored less than 3 days, good if stored less than 7 days, and unusable if stored more than 20 days.*

## 1.11 Accelerations and Vibration Limits

### 1.11.1 Quasi-steady Accelerations

*Less than* $1\mu g$ *with no preferred direction.*

### 1.11.2 $g$-jitter

*Less than* $100\mu g$ *(rms) over* $0.1 - 20Hz$.

### 1.11.3 Thruster Firings

Less than $1000\mu g$ for no longer than $0.1sec$, with total integrated firing times less than $1.8sec$ during a 5-hour period.

### 1.11.4 Cartridge Translator

Physical translation of the sample cartridge is not permitted while the samples are in the solid-liquid state.

### 1.11.5 Electromagnetic Limitations

The experiment should not be located next to equipment which generates magnetic fields in excess 0.5 Tesla external to the equipment and there should be no electrical current passing through the samples.

## 1.12 Data Acquisition

### 1.12.1 Temperatures (High Rate)

The temperature will be measured at 5 points within the sample holder.
Fine Mode: For temperatures greater than the eutectic temperature, recorded temperatures should be measured with a precision of 0.01K and an accuracy of 0.1K. The acquired and recorded data rate should be at least $1Hz$.
Coarse Mode: For temperatures below the eutectic temperature, and above 100°C recorded temperatures should be measured with a minimum precision of 0.1K and a minimum accuracy 1.0K. For temperatures below 100°C the recorded temperatures should be measured with a minimum precision of 0.2K and a minimum accuracy of 2.0K. The acquired and recorded data rate should be at least $1Hz$.

### 1.12.2 Temperatures (Low Rate)

For verification purposes, the temperature of each sample holder needs to be monitored prior to and following the experiment. The required precision of the measurement is 1.0K and the required accuracy is 2.0K. The absolute minimum

data rate required is one measurement per hour. This is sufficient as these measurements are monitoring the temperature of the unit during storage.

### 1.12.3 Acceleration

3-axis $1\mu g$ sensitivity over 0 to $20Hz$ range in frequency bands to be determined. Real time measurement of the acceleration is necessary. The measurements are to be made at a location as close to the experiment as possible.